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The Influence of the Laser Energy on the Thermal Diffusivity Evaluation of TBC by Laser Flash

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Laser Flash is considered the standard technique for measuring the thermal diffusivity of solids. The interaction between TBC and the laser energy is studied because very low thermal effusivity and thermal diffusivity of TBC can produce very high temperature increase on the surface and temperature gradient within the sample. In such a case, microstructural modifications of TBC can be generated. In this work, such phenomena are studied experimentally on free standing TBC samples.

Keywords laser flash, microstructure evolution, thermal barrier coatings

1. Introduction

Ceramic thermal barrier coatings (TBCs) are widely applied for protecting hot path components of gas turbines from combustion gases. The state-of-the-art TBC is represented by Yttrium oxide partially stabilized Zirconium (YPSZ) oxide (7-8 wt.% $Y_2O_3 + ZrO_2$) deposited onto the components either by Air Plasma Spray (APS) or by Electron Beam Physical Vapor Deposition (EB-PVD) (Ref 1). TBC microstructural features being related to the deposition process parameters and service conditions, to estimate the effective insulation performances of TBCs, the thermal conductivity of either new or aged/serviced TBC samples is often investigated. In fact, exposure to high temperature promotes sintering phenomena within the TBC by microcrack healing, by neck formation, and by reducing the very fine porosity, making the TBC less strain compliant and more thermally conductive.

Nowadays, Laser Flash (LF) is considered the standard technique for measuring the thermal diffusivity α of solids. This method consists in heating the front face of a sample by a short laser pulse and in detecting the temperature rise on its rear surface (Ref 2).

This technique has been extensively studied in the past, especially for all those effects that limit the reliability and the accuracy of measurements, such as finite pulse duration (Ref 3), heat radiation losses (Ref 4), nonuniform heating (Ref 5), sample thickness (Ref 6).

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Heterogeneous refractory materials such as ceramic coatings, composites, and foams represent critical cases according to the aforementioned uncertainties sources. This is particularly true for TBCs which are low conductive and usually thin (100-1000 μm).

Taylor et al. report the errors in thermal conductivity of TBC deposited onto metallic substrate calculated on the basis of the thermal diffusivity data, as given by LF measurements, considering the effects of errors in the input parameters (i.e., thickness, density and specific heat of coating and substrate, half-time, and substrate diffusivity) (Ref 7, 8).

Many authors reported the effects of IR detector nonlinearity as a function of temperature. In particular, linearity could be usually assumed when the temperature increase of the rear surface of the sample is kept within 5 °C (Ref 7, 9-11). Hasselman and Wang and Dinwiddie also considered the effect of the laser pulse energy on the thermal diffusivity measurement. A decrease of thermal diffusivity is reported for graphite and for two different APS porous ceramic coatings (Al_2O_3 and YPSZ) when the laser energy is increased. Authors attribute it to the IR detector nonlinearity effects caused by temperature increases higher than 5 °C (Ref 6, 10).

Hay et al. report an exhaustive analysis of uncertainties of thermal diffusivity by means of the LF technique, according to the ISO/BIPM "Guide to the expression of uncertainty in measurement." They consider the following five category uncertainty sources: measurement means, method, materials, medium, and manpower (Ref 11). As regards the first category, in the specific case of TBC (either free standing or on a substrate), the sample thickness should be highlighted. In fact, TBC is usually thin, not uniform, and difficult to measure.

An aspect that has not been explicitly pointed out in the literature is related to the interaction between TBC and the laser energy. In fact, since YPSZ TBCs have very low thermal effusivity values, when compared with metals, the maximum temperature increase of a sample front face due to the flash of the laser is many times that of a metallic sample (i.e., four times that of AISI304 austenitic steel), if the same energy pulse is absorbed. Furthermore, because of its very low thermal diffusivity (typically 3-6 $\times 10^{-7}$ m^2/s, in the as-sprayed condition or after a short aging time), the temperature gradient through the TBC sample thickness cannot be neglected for some milliseconds. This combined effect of high temperature increase and temperature gradient within the sample, if the mechanical properties (toughness) of the sample are low enough, could induce microstructural modifications of TBC in terms of either the growing or the reopening of microcracks (the main factor responsible for the thermal diffusivity reduction in porous coatings in respect to the bulk material). This effect is expected to be more evident the higher the single energy pulse absorbed by the sample. Moreover, the thinner the free standing TBC, the thicker, in percentage, the layer damaged by the LF pulse.

In this work, the results of experiments devoted to estimate the effect of the laser pulse energy on the microstructure modifications of TBC by measuring the thermal diffusivity are reported.

2. Theoretical Remarks

The asymptotic temperature increase of a one-dimensional adiabatic slab of thickness l heated at time $t=0$ by a spatially uniform Dirac pulse of energy density W is:

$$T_{\infty} = \frac{W}{\rho C l} \quad \text{(Eq 1)}$$

where ρ and C are the slab density and specific heat, respectively (Ref 12, 13).

The temperature increase of the front face of a sample during a LF experiment is directly proportional to the energy density W of the absorbed pulse and inversely proportional to the thermal effusivity ε of the material, as clearly described by:

$$T(0,t) = \frac{W}{\varepsilon\sqrt{\pi t}}\left(1 + 2\sum_{n=1}^{\infty} e^{-\frac{n^2 l^2}{\alpha t}}\right) \quad \text{(Eq 2)}$$

where α and t are the thermal diffusivity of the layer and the time, respectively (Ref 14).

From Eq 2 it is clear that a few instants after the heating pulse, the lower the thermal effusivity is, the higher will be the surface temperature, independently of the sample thickness.

If the finite duration τ of the pulse is considered, by approximating the pulse as a single square wave, the following equation could be used:

$$T(0,t) = \frac{2F}{\varepsilon\sqrt{\pi}}\left\{\begin{array}{l}\left[\sqrt{t}\left(1 + 2\sum_{n=1}^{\infty}\left\{\frac{e^{-\frac{n^2 l^2}{\alpha t}}}{\sqrt{\pi}} - \frac{nl}{\sqrt{\alpha t}}\operatorname{erfc}\left(\frac{nl}{\sqrt{\alpha t}}\right)\right\}\right)\right] \\ -2H(t-\tau)\sqrt{t-\tau}\left(1 + 2\sum_{n=1}^{\infty}\left\{\frac{e^{-\frac{n^2 l^2}{\alpha(t-\tau)}}}{\sqrt{\pi}} - \frac{nl}{\sqrt{\alpha(t-\tau)}}\operatorname{erfc}\left(\frac{nl}{\sqrt{\alpha(t-\tau)}}\right)\right\}\right)\end{array}\right\} \quad \text{(Eq 3)}$$

where F is the power density of the pulse and H and erfc are the Heaviside function and the complementary of the error function, respectively (Ref 12). Table 1 reports, for a fixed amount of absorbed energy, the temperature increase for different materials at different instants after the flash, as estimated by Eq 1 and 2.

It is worth noting that from the theoretical analysis, following Eq 2 and 3, for refractory materials such as YPSZ porous TBC, significant temperature increases of the front face of the sample are expected few instants after the flash.

3. Experimental

3.1 Samples

For evaluating the effect of the laser pulse energy on the microstructure of partially sintered TBCs, two free standing samples with different thicknesses and

Table 1 Estimated temperature increase for different materials at different instants after the flash for a fixed amount of absorbed energy

Material	Absorbed energy, J	Thermal conductivity, W/m K	Thermal diffusivity, m^2/s	Thermal effusivity, $J/Km^2 s^{1/2}$	Density, kg/m^3	Cp, J/kg K	Thickness, m	Asymptotic temperature Eq 1, K	Front face temperature increase 1 ms after the flash Eq 2, K	Front face temperature increase 2 ms after the flash Eq 2, K
YPSZ	1.0	1	4.0E−07	1583	5324	470	1.0E−03	5.1	143.6	101.6
AISI 304 stainless steel	1.0	16	4.0E−06	8000	8000	500	1.0E−03	3.2	28.4	20.1
ARMCO IRON	1.0	79	2.3E−05	16,648	7800	447	1.0E−03	3.7	13.7	9.7
Aluminum alloy	1.0	177	7.3E−05	20,709	2770	875	1.0E−03	5.3	11.0	7.8
OFHC Copper	1.0	399	1.2E−04	37,041	8933	385	1.0E−03	3.7	6.1	4.3

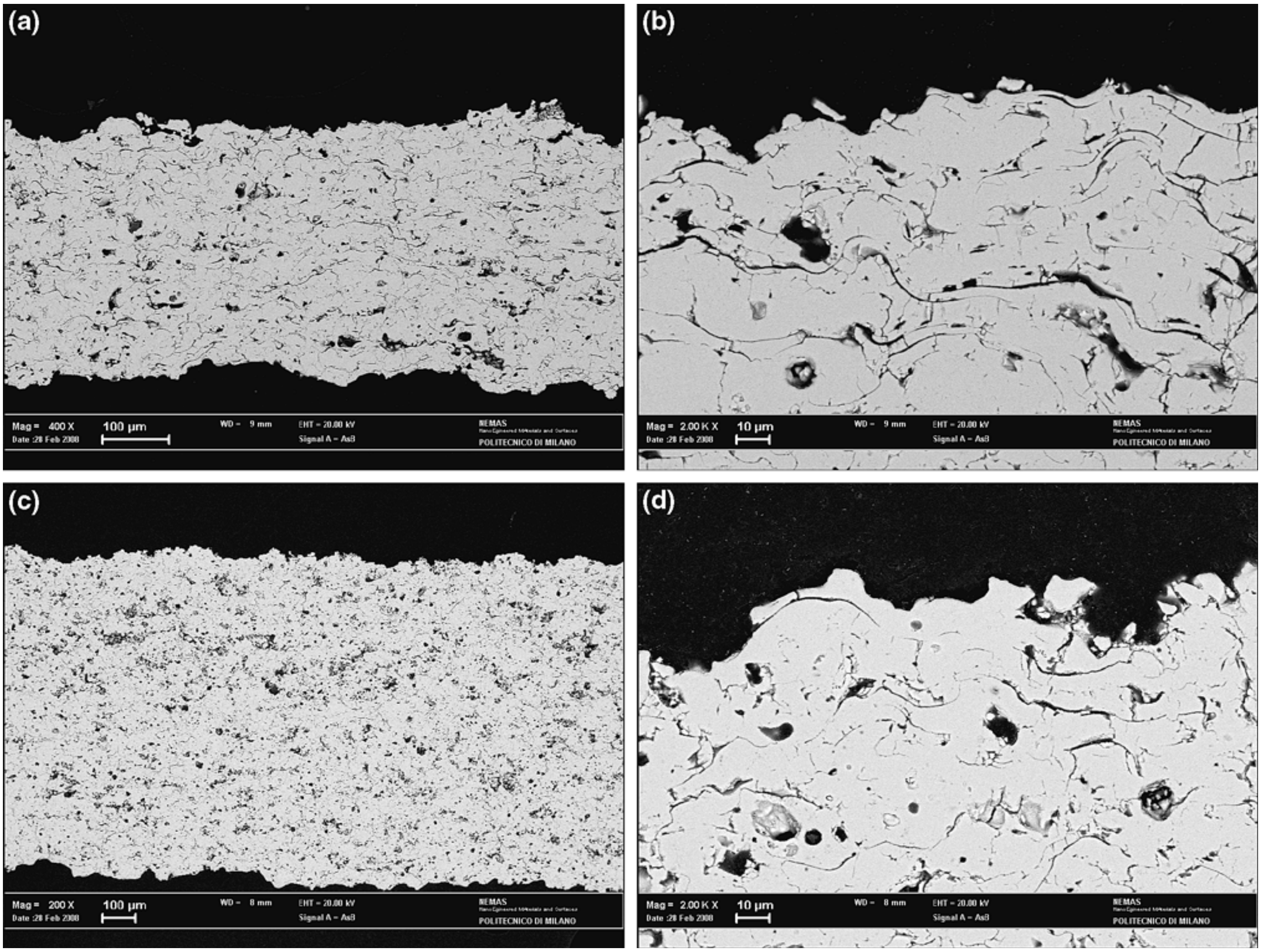

Fig. 1 Backscattered electron images at two different magnifications of the microstructure of: (a) and (b) sample 1 and (c) and (d) sample 2, respectively. The partial healing of microcracks produced by sintering phenomena can be clearly observed in the highest magnification images

Table 2 YPSZ APS TBC samples tested during the experimental activity

Sample	Condition	Thickness, μm	Porosity, %	Thermal diffusivity before laser damaging, 10^{-7} m^2/s	Thermal diffusivity after laser damaging, 10^{-7} m^2/s	Thermal diffusivity relative variation, %
1	Aged 15 h at 1250 °C	224 ± 18	12.1 ± 1.6	5.8 ± 0.5	4.2 ± 0.4	26.9
2	Aged 15 h at 1250 °C	18.3 ± 2.4	18.3 ± 2.4	5.0 ± 0.7	4.1 ± 0.4	17.2

microstructures (see Fig. 1) aged at 1250 °C for 15 h have been considered, as summarized in Table 2.

3.2 The LF Equipment

The through-thickness thermal diffusivity measurements were carried out on 10 mm diameter disk-shaped specimen by using a LF equipment (Theta Industries Inc., Port Washington, NY, USA) in vacuum ($<$0.01 Pa), at room temperature, where the maximum sensitivity of thermal diffusivity to the microstructure is expected.

A pulsed 1.06 μm wavelength Nd:YAG laser (Laser Metrics Winterpark FL-USA) is used for heating samples. The pulse energy can be tuned from 0.5 to 10 J. The beam shape is circular (12.7 mm diameter) with a uniform intensity.

To collect statistically meaningful data, measurements were repeated three times for each condition. Owing to the TBC translucency, prior to evaluating the thermal diffusivity, thin layers of colloidal graphite were painted on both sample surfaces to make the TBC front face opaque to the Nd:YAG laser radiation and to increase the rear face emissivity in the IR detector sensitivity range (3-5 μm).

Thermal diffusivity was estimated by inverting the experimental data using both the ratio and the Cowan

Table 3 Temperature increase on front face of a YPSZ APS TBC 500 μm thick, as estimated by equations in the text and thermal properties reported in Table 1

Absorbed energy, J	Front face temperature increase 1 ms after the flash by Eq 2	Front face temperature increase 2 ms after the flash by Eq 2	Maximum front face temperature increase Eq 3	Front face temperature increase 1 ms after the flash by Eq 3	Front face temperature increase 2 ms after the flash by Eq 3	Averaged temperature increase within the first 2 ms by Eq 3	Asymptotic temperature increase Eq 1	Expected dilatation for averaged temperature increase within the first 80 μm, μm
1.4	201	142	443	148	120	281	14	0.22
2.9	417	295	929	329	246	587	30	0.47
7.4	1056	747	2344	830	648	1496	75	1.20
10.0	1436	1016	3210	1143	894	2052	102	1.64

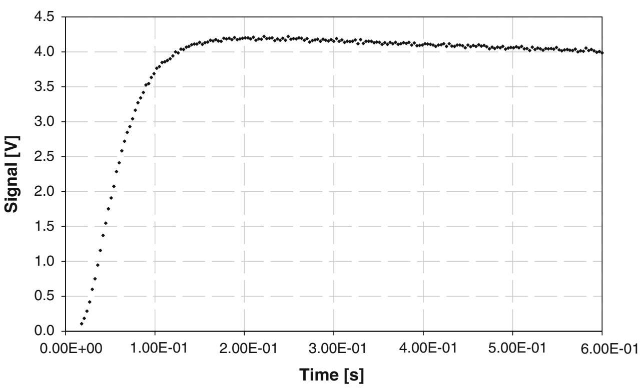

Fig. 2 Signal versus time as given by the IR detector for sample 1, during the LF measurement

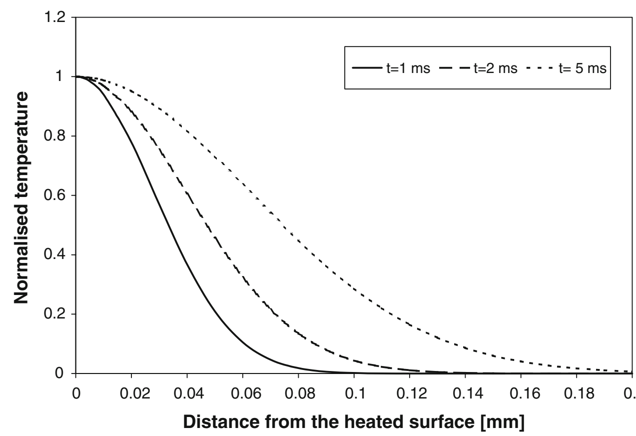

Fig. 3 Normalized temperature versus the through-thickness distance from the front surface of the sample, few instants after the flash. In particular, 2 ms after the flash the temperature increase is almost confined within the first 80 μm

methods accounting for radiation losses (Ref 15). Since the laser pulse duration τ was short enough (<800 μs) when compared with the characteristic experiment times ($t_{1/2}$ > 14 ms), no specific correction has been applied during data inversion.

4. Results and Discussion

To be sure to investigate only the effects of micro-structural permanent damages produced by high energy laser pulses within porous TBC, thermal diffusivity measurements have always been carried out using low energy (≅0.5 J) laser pulses for two reasons:

(1) not to damage the samples (i.e., repeated measurements furnish the same value of thermal diffusivity, within the experimental uncertainty). In fact, in this case, the temperature increase 2 ms after the flash on the front face is estimated to be slightly lower than 50 °C for both samples.
(2) to make the temperature increase on the rear face of the sample lower than 5 °C, as estimated by Eq 1.

Each thermal diffusivity measurement was performed only at a sufficiently long time after having heated samples by single high energy laser pulses, at the beginning of the experiment, and by bursts of pulses (three or four pulses fired at 2 s interval) later. The energy absorbed by the samples (except that of the LF measurement themselves) when heated by each single laser pulse is given in Table 3.

As in other LF equipments, the signal produced by the IR detector is a voltage increase (see Fig. 2) and no direct indications of the sample temperature are given. To be able to quantify the absorbed laser energy from the capacitor voltage, the asymptotic temperature increase of a AISI304 stainless steel specimen (see Table 1), with surface features similar to those of TBC samples, was measured using a snapshot focal plane array Infrared camera CEDIP Jade II (sensitivity region 7-9.6 μm, frame rate from 150 up to 2000 Hz). Thus, a rough estimation of the temperature increase for TBC samples has been performed theoretically using Eq 1.

Table 3 also gives the estimation of the temperature increase of both front and rear surfaces and the estimation of the expected maximum deformation induced within the first 80 μm of a typical YPSZ TBC sample, with thermal properties reported in Table 1, considering the time duration τ = 0.8 ms. The 80 μm thickness has been fixed considering the depth profile of the temperature 2 ms after the flash (see Fig. 3).

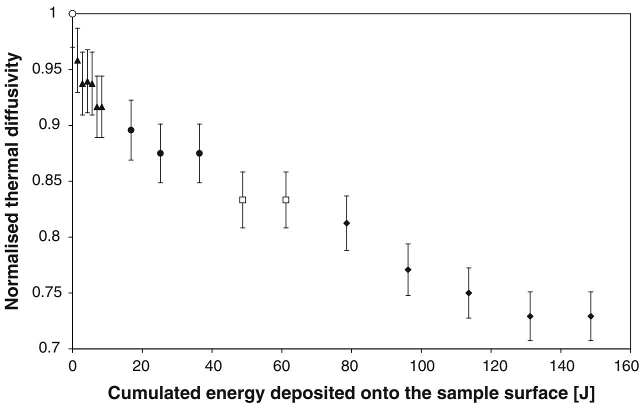

Fig. 4 Sample 1. Normalized thermal diffusivity versus the cumulated energy deposited onto the sample surface by the laser pulses. (▲), (●), (□), and (◆) refer to the heating produced by single laser pulses of 1.4 J and by bursts of three pulses (or four limited to the case of 2.9 J pulse) of 2.9, 7.3, and 10 J, respectively

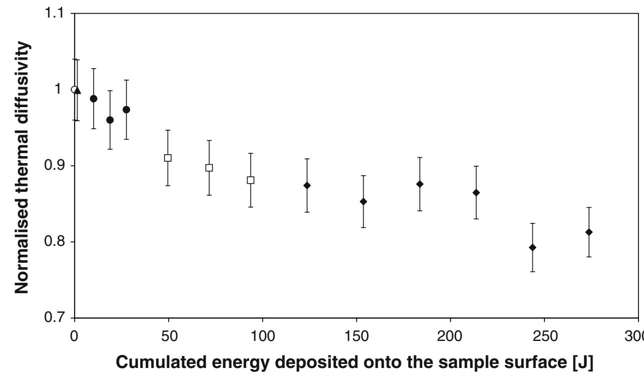

Fig. 5 Sample 2. Normalized thermal diffusivity versus the cumulated energy deposited onto the sample surface by the laser pulses. (▲), (●), (□), and (◆) refer to the heating produced by single laser pulses of 1.4 J and by bursts of three pulses of 2.9, 7.3, and 10 J, respectively

Taking into account that porous plasma-sprayed TBCs are characterized by spherical pores and microcracks mostly oriented parallel and perpendicular to the coating interface with typical crack thickness distribution in the range 0.02-1 μm, the thermally induced deformations, as estimated in Table 3, could promote reopening and growing of microcracks detectable as thermal diffusivity reduction (Ref 16-19).

The deformation has been estimated assuming:

- The thermal expansion coefficient of YPSZ = 1×10^{-5} °C^{-1};
- The temperature increase inside the 80 μm thick layer facing the laser radiation as the average value of the temperature profile shown in Fig. 3.

The temperature inside the sample, except the front layer is equal to room temperature.

Figure 4 and 5 show the thermal diffusivity, normalized in respect of its initial value (i.e., before the damaging procedure) of the two samples, respectively, as a function of the cumulative absorbed energy, assuming the energy of laser pulses being repeatable. It is worth noting that after some bursts of a fixed energy (Fig. 4), thermal diffusivity does not change anymore even if other pulses of the same energy have been fired. It means that the damage level of the microstructure did not change. A possible explanation is that a higher energy is required to generate a more significant deformation able to promote further microstructural damage within each sample. To confirm this interpretation, when no thermal diffusivity reduction is observed between consecutive heating pulses, the energy density of each pulse is elevated and a further reduction of the thermal diffusivity is experienced, as shown in Fig. 4 and 5.

As expected, for the thick TBC sample, the normalized damaging effect of pulses is less evident when compared with the thinner sample, because the damaged layer for the thick sample is thinner in respect to its whole TBC thickness.

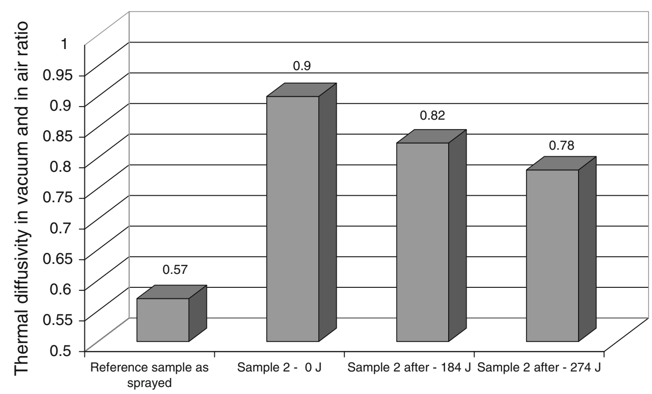

Fig. 6 Ratio of the thermal diffusivity measured in vacuum and in air for sample 2. Note that to an increase of the cumulated energy corresponds a reduction of this ratio caused by microstructure damage by the energy pulses. For comparison purposes, the corresponding ratio for a thick porous TBC in the as-sprayed condition is also reported. The effects of high temperature exposure are clearly pointed out as a significant increase of this thermal diffusivity ratio

To confirm that the observed thermal diffusivity decrease is related only to microstructural modifications, for sample 2, the thermal diffusivity has been measured not only in vacuum but also in air, at the beginning of the experiment and after having cumulated energy of 184 and 274 J. Figure 6 summarizes these measurements giving the ratio between in-vacuum and in-air thermal diffusivity. The decrease of this ratio could be ascribed, as explained elsewhere (Ref 20), only to the promotion of microcrack nucleating and growing within the TBC. In this specific case, the decrease is caused only by laser pulse microstructural damaging, excluding all the other possible modifications that can happen to this material, when exposed to high temperature (phase transformations, chemical reactions, etc.). For comparison purposes, the value of this ratio was estimated also for a thick porous TBC sample in the as-sprayed conditions, as reference.

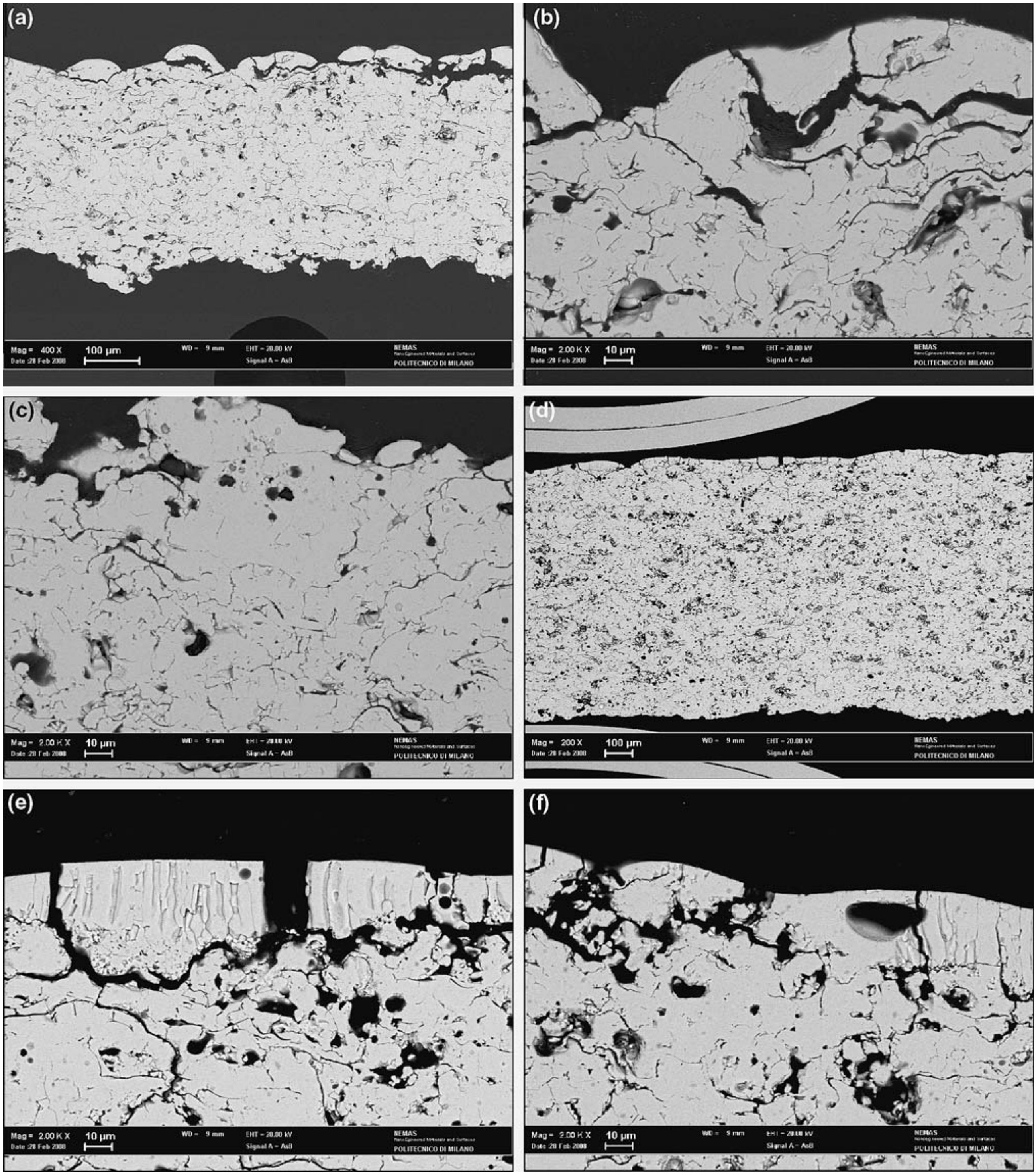

Fig. 7 Backscattered electron images of the microstructure of laser damaged (a), (b), and (c) sample 1 and (d), (e), and (f) sample 2, at two different magnifications

Because of its high porosity content, the sample in the as-sprayed condition shows a value of 0.57 for this ratio in respect of typical values of less porous TBC samples ranging from 0.63 to 0.67 (Ref 21). It is also interesting to note that after 15 h at 1250 °C a very significant variation of this ratio can be observed. This confirms the low activation energy of sintering of TBC, as also reported in the literature (Ref 20, 22, 23). Notwithstanding the high porosity content of sample 2, the ratio of thermal diffusivities raises to about 0.91. In fact, during the first few hours, sintering involves mainly splat boundaries and microcracks that, from a volumetric point of view, represent a negligible percentage of the overall porosity content, but, from the heat conduction through the TBC, play a major role. Furthermore, some spheroidal pores could be close thus not contributing to the thermal diffusivity variations as a function of measurement atmosphere (Ref 20, 23, 24). Furthermore, for both samples, Fig. 7 clearly highlights the damage produced by the laser pulses on the first thin layer of the TBC samples. In particular, for both samples, close to the damaged surface, wide cracks almost parallel to the surface, and above them, thin TBC layers either sintered (Fig. 7a, b) or partially melted (Fig. 7d, e), can be observed. In particular, the presence of partially remelted layers 20-30 μm thick can be caused by the not perfectly homogeneous distribution of the energy of the laser beam on the sample surface, thus creating some spots characterized by energy density high enough to melt the YPSZ when the maximum pulse energy (10 J) is fired. Moreover, especially where no remelting happened (Fig. 7c, f), the width of microcracks appear to be wider than those of sound samples, as shown in Fig. 1.

Thus, for this type of porous refractory materials, in free standing conditions, to avoid modifications of sample microstructure, it is necessary to use a heating pulse delivering as low energy as possible. On the other hand, the heating pulse should give a signal high enough to detect on the rear surface the temperature increase needed for the thermal diffusivity evaluation. Since each laser has a energy threshold below which no flash is emitted, in some cases an attenuator should be used to keep the energy below the damage threshold.

5. Conclusions

Laser flash technique is a powerful technique for measuring the thermal diffusivity of solids at RT as well as at high temperature. To avoid any permanent damage of the sample when a LF measurement is carried out on brittle materials, characterized by very low values of thermal diffusivity, thermal effusivity, and toughness, as the case of freestanding APS TBC samples, the energy density deposited onto the sample surface should be minimized. In the most recent and advanced LF equipments, the energy of the laser pulse can be automatically minimized. When equipments leaving higher freedom degrees to the researcher are used, some analysis of the potential risks of damaging samples during the measurement should be carried out, preventively.

In this work, the damaging effect of the energy deposited on the surface of free standing TBC samples during LF measurements was experimentally investigated. The damage was evaluated experimentally and analyzed by suitable heat conduction modeling. For porous ceramics coatings, the condition of keeping the temperature rise on the rear face below 5 °C appears not to be sufficient for guaranteeing the thermal diffusivity measurement by LF method to be completely nondestructive. In particular, the lower the thermal effusivity and the thicker the thickness of the free standing sample, the lower should be the asymptotic temperature increase on the rear face to preserve the sample from damaging. The results of this study can also be extended also to other pulsed photothermal techniques applied to measure the thermal diffusivity of TBC-coated components.

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